

NASA-TM-112748

1115

7N-26-TM
000001

FORMATION OF ALUMINUM NITRIDE DURING CRYOMILLING OF NIAL

B.J.M. Aikin, R.M. Dickerson, D.T. Jayne
Case Western Reserve University, Cleveland, OH 44106

S. Farmer and J.D. Whittenberger
NASA Lewis Research Center, Cleveland, OH 44135

(Received June 2, 1993)
(Revised September 29, 1993)

Introduction

Prealloyed NiAl powders were milled in liquid nitrogen, a process known as cryomilling [1]. The materials, formed by extrusion or hot isostatic pressing the cryomilled powders, exhibit higher creep strengths than unreinforced NiAl during slow strain rate compression testing [2-7]. The increased strength was attributed to the presence of approximately 10 volume percent AlN particles which were dispersed along the NiAl prior particle boundaries [2,6]. The presence of AlN particles within a NiAl matrix was not expected based on previous cryomilling work with oxide dispersion strengthened (ODS) nickel and iron alloys by Petkovic-Luton and Vallone [8,9]. The experiments of Luton, et al. [1] on ODS aluminum alloys indicated that reactions between liquid nitrogen and aluminum were possible and led to Al(O,N) particles. The hypothesis of Luton, et al. [1] for the formation of the aluminum oxy-nitrides and the absence of AlN x-ray diffraction peaks in the spectra from as-cryomilled NiAl powders [2,4,5] convinced researchers that: 1) the nitrogen exists as an interstitial or solid solution element in NiAl after cryomilling, and 2) AlN precipitates during subsequent thermomechanical processing of the powders.

Recent work suggests that this hypothesis is not correct. In an effort to establish the nature of nitrogen in cryomilled NiAl, cryomilled powder particles have been subject to bulk chemical analyses, x-ray diffraction analyses, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Evidence supporting the existence of AlN formation on the surface of cryomilled NiAl powders is presented in this paper.

Experimental Procedure

Cryomilled NiAl powders from Exxon Research and Engineering Co. (Exxon) and NASA Lewis Research Center (LeRC) were used in this study. Two cryomilling runs were made at Exxon using the same original lot of prealloyed NiAl powder (P541). The chemistry for the original powder is given in Table 1. The milling parameters are outlined in reference [2]. Batch "mit" was cryomilled with a 0.5 wt.% Y_2O_3 , while batch "ohne" was milled without yttria (Y_2O_3). The compositions of the cryomilled powders are also shown in Table 1. After milling, both batches of powder were placed in a dry box as the liquid nitrogen boiled off. The cryomilled powder was removed from the grinding media by sieving. The powders were then packed in plastic bottles under an argon atmosphere and shipped to LeRC. All subsequent handling was done in air.

At LeRC, friable melt spun NiAl ribbon (2013, Table 1) was autogenously crushed in a plastic bag and used as the charge for an 01-HD attritor. The attritor was loaded with a 12:1 ball to powder weight ratio mixture and the NiAl was cryomilled for 8 hours at 660 RPM. The grinding media was separated from the cryomilled powder (CM2013) by sieving the slurry into dewars. A specimen from the CM2013 powder slurry was directly transported to an XPS facility. Another specimen from this powder was then heat treated at 1505 K for 2 hours in a dynamic argon atmosphere to simulate the thermal portion of a typical densification procedure. X-ray diffraction patterns were obtained using copper $K\alpha$ radiation for both the cryomilled and heat treated powders produced at LeRC.

The surface chemistry of the original and cryomilled NiAl powders were investigated using XPS. This instrument analyzes the top several monatomic layers of a sample, providing both elemental and chemical state information [10]. The photoelectron binding energies (corrected for charging) were used to determine the chemical state of elements present within 0-4 nm of the powder particle surface. The Exxon powders were pressed into indium foil in order to prevent charging during analysis. The LeRC cryomilled powder, while still in liquid nitrogen, was placed into a nitrogen purged glove bag which was attached to the entry port of the XPS analysis system. An XPS

sample cup was dipped into the powder slurry and immediately placed under vacuum. The powders were examined by XPS after evaporation of the liquid nitrogen.

TEM specimens were prepared using two methods: 1) cryomilled powder particles were dispersed onto grids so that thin edges of small particles could be directly viewed, and 2) some of the cryomilled powders were mounted in epoxy, sliced, dimpled and ion milled in order to obtain electron transparent areas for analysis.

Results and Discussion

The bulk chemical data for the starting and cryomilled powders are given in Table 1. In general, cryomilling increased the nitrogen, oxygen, carbon and iron contents. The increase in iron and part of the carbon contamination are believed to come from wear of the steel grinding balls, impeller and tank during milling. The oxygen and additional carbon came from handling the powders in air and from impurities in the liquid nitrogen. The nitrogen content is negligible in the starting materials but increases to 2-6 at.% during cryomilling. The LeRC batch 2013 contained a high level of silicon due to contamination from the mold material during induction melting. The cryomilled powder CM2013 had a much higher oxygen content than what is normally produced by this method. The cause of the high oxygen content is not known.

TABLE 1.
Bulk Concentrations of Starting and Cryomilled Materials in Atomic Percent.

Material	Al	N	O	C	Fe	Si	Y	Ni
P541	50.30	<0.01	0.02	<0.01	0.08	-	-	bal
Ohne	46.75	5.87	1.28	0.03	0.07	-	-	bal
Mit	47.44	4.57	1.25	0.05	0.08	-	0.16	bal
2013	50.94	<0.01	0.02	0.01	<0.01	0.15	-	bal
CM2013	43.59	2.38	6.46	0.34	0.15	0.15	-	bal

In agreement with previous work [2,5], x-ray diffraction patterns of cryomilled powders contain NiAl peaks only (Figure 1). After a 2 hour anneal at 1505 K in argon, however, peaks for both AlN and Al₂O₃ are clearly present. Heat treatment also decreases the width of the NiAl diffraction peaks, indicating a loss of residual strain and/or grain growth.

XPS was performed in order to determine the state of the nitrogen on the cryomilled powders since AlN peaks were not detected unless the powders were heat treated or thermomechanically processed. Results from the XPS analyses of the three lots of cryomilled NiAl are presented in Table 2. The binding energy of the nitrogen 1s photoelectron indicates that nitrogen is only present as a nitride, presumably only AlN. Oxygen and adventitious carbon were also found. The oxygen was mostly in the form of Al₂O₃ and nickel oxides were not found. AlN on the surface of the sample was oxidized to form native Al₂O₃. The Al₂O₃ on the surface attenuates the nitrogen 1s signal from the remaining AlN below it. The Al₂O₃:AlN ratio in the near surface region of the powder depended upon the subsequent exposure of AlN to oxygen. This explains why the highest surface content of AlN was found in CM2013, the specimen that had been transported to the XPS facility in the original liquid nitrogen. In summary, XPS results indicate the presence of AlN in the near surface region for all three cryomilled powders examined.

TABLE 2.
Chemical Compositions of the Powder Surfaces Determined During XPS Analyses, at. %.

Material	Ni	Al	N	O	C	Y	Si
P541	5.3	24	-	48	23	-	-
Ohne	16	14	4.0	56	11	-	-
Mit	15	18	5.4	53	8.1	<0.22	-
CM2013	16	35	7.2	41	<1	-	-

Transmission electron microscopic analyses of the CM2013 powder revealed micrometer and sub-micrometer sized particles consisting primarily of very fine grained (5-100 nm) mixtures of NiAl and AlN (Figure 2). The fine multiphase structure was also seen in the edges of the powder particles produced by Exxon (Figure 3). Selected area electron diffraction ring patterns taken from multiphase regions contained reflections for AlN in addition to strong NiAl reflections. Some diffraction evidence for larger NiAl grains was obtained as well, although none of the larger grains were sufficiently electron transparent for clear imaging. No clear evidence for alumina was found in the areas examined. However, XEDS (x-ray energy dispersive spectrometry) and EELS (electron energy loss spectrometry) analyses performed in the TEM confirmed the presence of O and N in the mixed phase areas.

The solubility of nitrogen in NiAl is unknown but less than 900ppm based on recent work [11]. Also, no AlN particles were found within NiAl grains after thermomechanical processing as would be expected from a precipitation reaction [2-7]. Instead, particle free NiAl grains surrounded by a mantle of NiAl interspersed with AlN and oxide particles are observed after the cryomilled NiAl was consolidated [2-7]. We propose that most, if not all, of the AlN is formed as a very fine reaction product on the surface of the NiAl powder particles during cryomilling or during heating from 77 to 300K.

Summary

TEM and XPS results show that AlN and Al_2O_3 exist on powder particle surfaces of cryomilled NiAl. AlN and Al_2O_3 present on the powders coarsen to a size detectable by x-ray diffraction during heat treatment or thermomechanical processing.

References

1. M.J. Luton, C.S. Jayanth, M.M. Disko, S. Matras and J. Vallone, *Multicomponent Ultrafine Microstructures*, eds. L.E. McCandish, B.H. Kear, D.E. Polk and R.W. Siegel, Mater. Res. Soc. Symp. Proc., **132**, MRS, Pittsburgh, PA (1989) 79-86.
2. J.D. Whittenberger, E. Arzt and M.J. Luton, *J. Mat. Res.*, **5** (1990) 271-277.
3. J.D. Whittenberger, E. Arzt and M.J. Luton, *Intermetallic Matrix Composites*, eds. D.L. Anton, R. McMeeking, D. Miracle and P. Martin, Mater. Res. Soc. Symp. Proc., **194**, MRS, Pittsburgh, PA(1990) 211-217.
4. J.D. Whittenberger, E. Arzt and M.J. Luton, *J. Mat. Res.*, **5** (1990) 2819-27.
5. J.D. Whittenberger, *Solid State Powder Processing*, eds. A.H. Clauer and J.J. deBarbadillo, TMS, Warrendale, PA (1990) 137-155.
6. J.D. Whittenberger, E. Arzt and M.J. Luton, *Scripta Metall. Mater.*, **26** (1992) 1925-30.
7. J.D. Whittenberger and M.J. Luton, *J. Mat. Res.*, **7** (1992) 2724-2732.
8. R. Petkovic-Luton and J. Valone, U.S. Patent 4,619,699 (1986).
9. R. Petkovic-Luton and J. Valone, U.S. Patent 4,647,304 (1987).
10. J.T. Grant, *Surf. Interface Anal.*, **14** (1989) 271-283.
11. R. Noebe and A. Garg, unpublished research, NASA Lewis Research Center, Cleveland, OH.

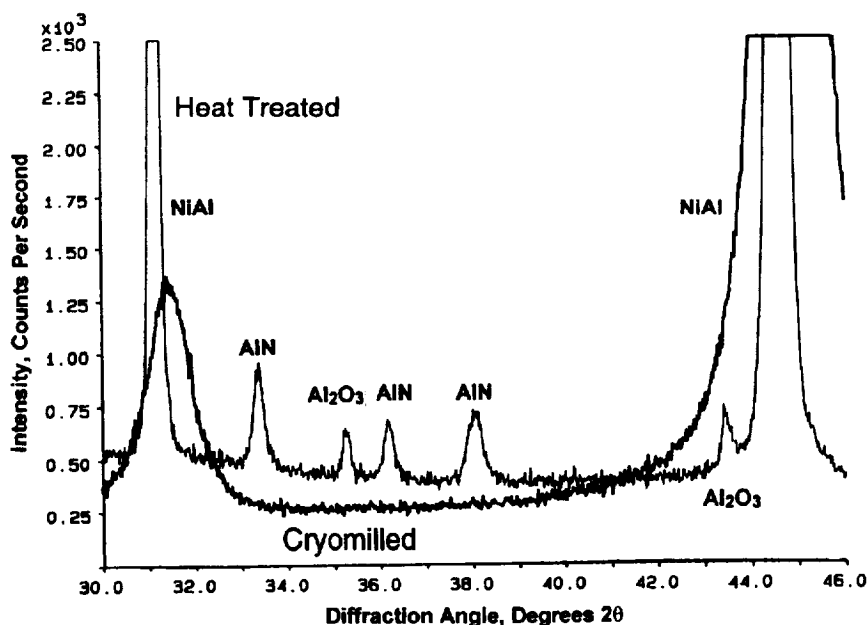


FIGURE 1. X-ray diffraction scans for cryomilled NiAl (CM2013) as milled and after heat treatment at 1505 K for 2 hours under argon.



FIGURE 2. TEM photomicrograph of a NiAl cryomilled powder particle (CM2013) showing a cross section of the surface layer indicating a mixture of NiAl and AlN grains.

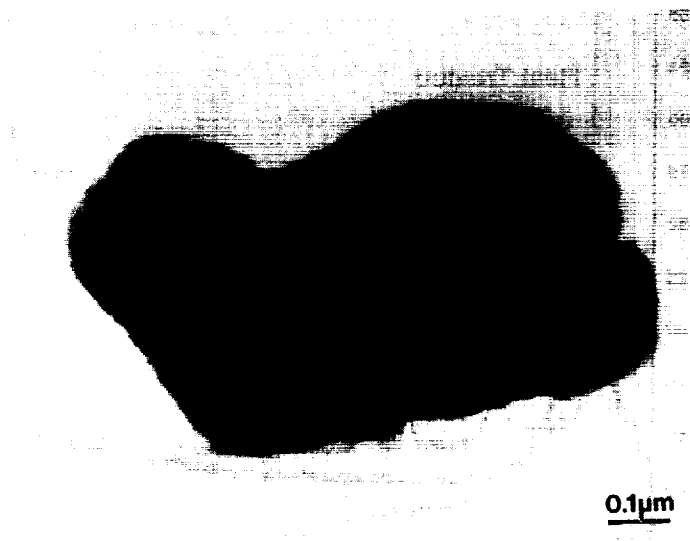


FIGURE 3. TEM photomicrograph of a small NiAl cryomilled powder particle (Ohne) showing a mixture of NiAl and AlN grains at the edges.